(19) RU (11) 2156650 (13) C1
(51) 7 B 01 J 8/20, C 07 C 1/06

RUSSIAN AGENCY ON PATENTS AND TRADEMARKS
(12) DESCRIPTION OF INVENTION
to Russian Federation Patent

(21) 98123706/12 (22) 12.30.1998
(24) 12.30.1998
(46) 09.27.2000, Byul. No. 27
(72) Anikeev V. I. (RU), Ermakova Anna (RU)
(71) (73) G. K. Boreskova Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (RU)
(56) D. B. BUKUR et al., Fixed bed and slurry reactor studies of Fischer–Tropsch synthesis on precipitated iron catalyst, *Appl. Catal.*, **61**, 329-349 (1990). I. A. ALEKSANDROV, *Distillation and Fractionation in Petroleum Refining*, Khimiya, Moscow (1981), pp. 334-342. SU 701529 A (11.30.1979). US 423265 A (12.27.1983). US 4471145 A (09.11.1984). GB 2323029 A (03.1990). US 5506272 A (03.19.1996).
(98) 630090 Novosibirsk, Pr. Akademika Lavrent'eva 5, G. K. Boreskova Institute of Catalysis, Patent Department, T. D. Yulinoi

(54) METHOD OF CONDUCTING FISCHER-TROPSCH SYNTHESIS (VARIANTS) AND METHOD OF SELECTING A CONSTANT SOLVENT COMPOSITION IN A SLURRY REACTOR

(57) The invention concerns the field of chemical engineering and can be used for synthesis of saturated and unsaturated hydrocarbons with preliminary separation of multicomponent, multiphase mixtures at the reactor outlet into fractions of the desired composition, formation of a constant liquid reaction medium, and optimization of the Fischer–Tropsch process. CO and H_2 are fed into a reactor containing the liquid solvent with the catalyst suspended in it,

condensed products of synthesis are returned to the reactor, and the component composition of the condensate returned to the reactor is varied by changing the temperature in the reflux condenser or changing the proportion of condensed products of the reaction returned to the reactor to an amount that does not exceed the total amount of condensed products from the reactor outlet. The amount and composition of the liquid products returned to the reactor are adjusted to maintain a constant solvent composition. 3 s.p. f., 1 table, 3 fig.

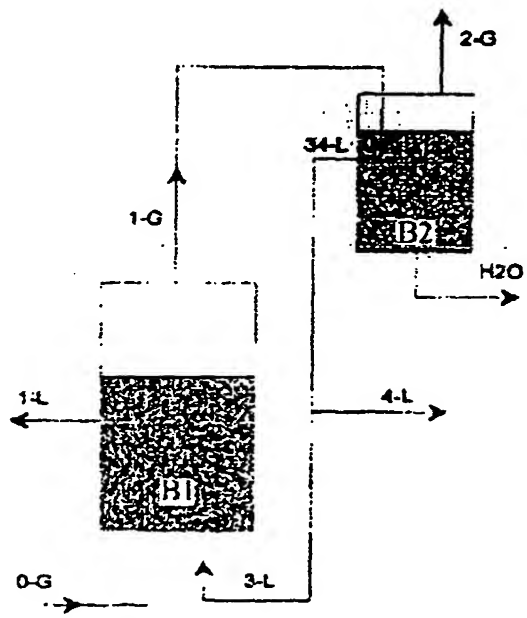

Fig. 1

The invention concerns the field of chemical engineering and can be used for synthesis of saturated and unsaturated hydrocarbons with preliminary separation of multicomponent, multiphase mixtures at the reactor outlet into fractions of the desired composition, formation of a constant liquid reaction medium, and optimization of the Fischer–Tropsch process.

The proven and projected natural gas reserves are now significantly higher than the crude oil reserves, so that the creation of new, complex technologies for processing synthesis gas into liquid motor fuels and synthesis of olefins and paraffins is a very pressing problem in the world, including in Russia. In addition, Fischer–Tropsch synthesis is still the only effective method of producing heavy paraffins and is the basic process for production of hydrocarbon fuels from natural gas.

Modern methods of creating new technologies and conducting processes are based on the principles of mathematical modeling. Using current knowledge of the physicochemical principles of a process (principles of catalysis, kinetic characteristics of complex reactions, thermodynamics of phase transitions), and computer analogs of process schemes and processes are created and allow efficiently optimizing the technology in the planning stage and selecting its most efficient versions and methods of implementation.

The synthesis reactor is a key element in the technology for production of hydrocarbon fuels in the Fischer–Tropsch process. The catalytic process in the reactor determines the specifications for the initial feedstock and consequently defines the fundamental elements in synthesis gas production technology. The complex composition of the products obtained in the reactor in turn dictate the selection of the basic process stages which should follow the reactor unit.

Several varieties of catalytic reactors and methods of implementation are currently used in industry for FT synthesis. Increasing attention has recently been focused on the method of conducting the process in a reactor with a three-phase slurry bed, the so-called slurry reactor process, especially since the advantages of this method became clear during its industrial implementation at a SASOL II plant [C. N. Satterfield and G. A. Huff, Usefulness of a slurry-type Fischer–Tropsch reactor for processing synthesis gas of low hydrogen-carbon monoxide ratios, *Can. J. Chem. Eng.*, **60**, No. 1, 159-162 (1982); X. Lang, A. Akgerman, and D. B. Bukur, Steady-state Fischer–Tropsch synthesis in supercritical propane, *Ind. Eng. Chem. Res.*, **34**, No. 1, 72-77 (1995); B. Jager and R. Espinosa, Advances in low temperature Fischer–Tropsch synthesis, *Catalysis Today*, **23**, 17-28 (1995)].

There is a method for formation of a solvent from the liquid products of FT synthesis in a slurry reactor that we use as an analog [X. Lang, A. Akgerman, and D. B. Bukur, Steady-state Fischer–Tropsch synthesis in supercritical propane, *Ind. Eng. Chem. Res.*, **34**, No. 1, 72-77 (1995); B. Jager and R.

Espinosa, Advances in low temperature Fischer–Tropsch synthesis, *Catalysis Today*, **23**, 17-28 (1995); H. H. Storch, N. Golumbic, and R. B. Anderson, Wiley, New York (1951); S. C. Saxena, Bubble column reactors and Fischer–Tropsch synthesis, *Catal. Rev.-Sci. Eng.*, **37**, No. 2, 227-309 (1995)].

The method of implementation of Fischer–Tropsch synthesis in a reactor of this type consists of feeding the initial synthesis gas into the liquid products of the reaction in the solvent (henceforth "solvent") in which the catalyst is suspended. The initial synthesis gas in the form of bubbles passes through the suspension where it reacts on the catalyst with formation of light and heavy hydrocarbons and water. The heavy hydrocarbons basically remain in the liquid phase and are removed from the reactor together with the solvent and catalyst in an amount that ensures a constant level of solvent in the reactor. The light and some of the heavy hydrocarbons, unreacted gases, and water are removed form the reactor with the outgoing gas and enter separation units. A complicated processing unit is used for separation of the hydrocarbons formed into light motor oils and diesel and heavy cuts and for removal of water.

Thee is another method of implementing the process and forming the solvent in a Fischer–Tropsch reactor which we use as prototype [D. B. Bukur, S. A. Patel, and X. Lang, Fixed bed and slurry reactor studies of Fischer–Tropsch synthesis on precipitated iron catalyst, *Appl. Catal.*, **61**, 329-349 (1990)]. This method is implemented in a slurry reactor of the three-phase reactor class – gas-liquid-solid catalyst. In this reactor, the finely disperse catalyst is suspended in the liquid phase, and the catalyst particles are maintained in a pseudofluidized state by mixing the liquid phase with gas bubbles and a stirrer. The vapor–gas phase containing unreacted CO and H_2 with unsaturated vapors of the products of the reaction leave the reactor and enter the condenser where the high-boiling products of the reaction are condensed at the condenser temperature and returned to the slurry reactor.

The following are drawbacks of the prototype.

1. The amount of condensate returned to the reactor is not regulated and is a function of the condenser temperature and reaction rate.

2. A constant solvent composition is only formed by selection of the initial composition of the initial solvent and the temperature and pressure in the reactor, but since the temperature and pressure in gas-liquid systems are mutually dependent parameters, it will only be possible to control one of them, and only within a narrow range of variation.

The invention solves the problems of creating a method for preliminary separation of the products of the reaction of Fischer–Tropsch synthesis at the reactor outlet into several hydrocarbon-containing fractions and the method of forming a constant solvent composition.

The problems of preliminary separation are solved: by regulation of the condensed products (reflux) returned to the reactor in an amount no greater than the total amount of condensed products from the reactor outlet; by variation of the component composition of the returned condensate.

The problem of forming a constant solvent composition that ensures the required selectivity and output of the target hydrocarbon fraction is solved by selection of the amount and composition of the liquid product returned to the reactor.

A skeleton diagram illustrating the method of separation and forming of the solvent composition during the Fischer–Tropsch synthesis reaction is shown in Fig. 1. Here the synthesis gas, stream 0-G, with a fixed CO/H_2 ratio is fed into the synthesis reactor (unit B1). The return stream of condensate 3-L obtained in the reflux condenser (unit B2) goes in after elimination of water.

The vapor-gas stream 1-G after the reactor enters the reflux condenser for cooling. Part of the products of synthesis is condensed here at the reflux condenser temperature (T_2). The component composition of the condensate formed is rigorously related by phase equilibrium to the temperature. The liquid hydrocarbon fraction 34-L formed is separated into two parts: stream 3-L and stream 4-L. The first part is returned to the reactor and the second part, stream 4-L, is fed for further processing. The ratio of reflux stream 3-L to stream 34-L is defined by coefficient β. This parameter, like the reflux condenser temperature T_2, which alters the composition of the condensate, are the controlling process parameters.

In the conditions of synthesis, at temperatures of 530-550 K, the dry synthesis gas entering the reactor is continuously saturated with hydrocarbon vapors which go out of the reactor together with the gaseous products of the reaction. As a result, with high evaporation, flow of 1-L can become negative, which is equivalent to a continuous decrease in the volume of liquid-solvent in the reactor. The reflux stream compensates entrainment of liquid phase from the reactor and ensures a constant composition of the liquid phase in the reactor.

The parameters of the process for which the calculations were performed and examples were obtained are reported in Table 1. Such parameters as the temperature, pressure, space velocity, and H_2/CO ratio in the initial gas are kept constant.

The essence of the invention is illustrated by the following examples.

Example 1. Octacosane ($C_{28}H_{58}$) with a melting point of 334.3 K and boiling point of 610 K is used as the initial solvent in the reactor.

Coefficient β, which determines the fraction of returned condensate – stream 3-L – , varies. The condensation temperature in the reflux condenser is set equal to 373 K.

The distributions of hydrocarbons by fractions in the outgoing streams for β = 1 and β = 0.5 are shown in Fig. 2a, b. For β = 1, two target streams going out of the reactor are formed: a liquid stream (1-L) and a vapor-gas stream after the reflux condenser (2-G). For 1 > β > 0, the number of outgoing streams is equal to three, since the part of stream (4-L) not returned to the reactor is added to the preceding two streams.

The case of β = 1 in Fig. 2a will be examined. Distinct separation of the spectra into light and heavy fractions is seen in the outgoing streams. In contrast to the open scheme, the reflux thus makes it possible to obtain separation into light and heavy hydrocarbon fractions.

In the case of β < 1, Fig. 2b, as noted above, three fractions of intermediate product clearly separated into light, medium, and heavy hydrocarbons are removed. The amount of reflux thus affects separation of the hydrocarbon products of synthesis into fractions.

Example 2. The composition of the returned condensed products is varied by changing the temperature in the reflux condenser at which the vapor-gas going out of the reactor is condensed. The distributions of hydrocarbons by fractions in streams 2-G, 4-L, and 1-L going out of the reactor at three reflux condenser temperatures: 373 K, 423 K, and 473 K, respectively, and β = 0.5 are shown in Figs. 2b and 3a, b. It follows form the diagrams that separation becomes more distinct and the spectra of heavy and light hydrocarbon fractions diverges in different directions even more when the composition of the condensate is changed as a result of increasing the reflux condenser temperature. The degree of separation of the products at the Fischer–Tropsch synthesis reactor outlet is thus affected by varying the composition of the condensate returned to the reactor.

Example 3. The component composition and fraction of liquid hydrocarbons returned to the reactor are regulated to select the constant composition of solvent in the slurry reactor for Fischer–Tropsch synthesis. Since the fractional composition of outgoing stream 1-L from the reactor corresponds to the fractional composition of the solvent, it follows from Figs. 2a, b and 3a, b that regulation of the fraction of liquid hydrocarbons and the component composition of the liquid hydrocarbons returned to the reactor will change the composition of the solvent.

As the examples show, the proposed method allows separating the products of the reaction of Fischer– Tropsch synthesis at the reactor outlet into

several hydrocarbon-containing fractions and forming a constant solvent composition.

CLAIMS

1. Method of conducting Fischer–Tropsch synthesis in a slurry reactor, comprising feed of CO and hydrogen gases into a reactor containing a liquid solvent with a catalyst suspended in it and returning the condensed products of synthesis into the reactor, characterized by the fact that the component composition of the returned condensate is changed by changing the temperature in the reflux condenser.

2. Method of conducting Fischer–Tropsch synthesis in a slurry reactor, comprising feed of CO and hydrogen gases into a reactor containing a liquid solvent with a catalyst suspended in it and returning the condensed products of synthesis to the reactor, characterized by the fact that the fraction of condensed products of the reaction returned to the reactor varies in an amount not exceeding the total amount of condensed products from the reactor outlet, which alters the component composition of the condensate returned to the reactor.

3. Method of selecting a stable fractional composition of solvent in a slurry reactor for Fischer– Tropsch synthesis, comprising return of condensed products of synthesis, characterized by the fact that the component composition of the liquid products of the reaction returned to the reactor is regulated and the fraction of liquid products of the reaction returned to the reactor is regulated in the amount necessary for maintaining a constant solvent composition.

TABLE 1. Summary Information on the Process

Reaction temperature	K	533
Pressure	MPa	2.0
Space velocity	nm^3/kg cat./h	0.68
CO/H_2 ratio	--	1.0
Conversion of CO	%	35.84-37.47
Conversion of H_2	%	76.14-78.97
Total yield of hydrocarbons	kg/kg conv. CO	0.50
CH_4	wt. %	3.53
C_2-C_4	"	12.93
C_5-C_{11}	"	55.61
C_{12}-C_{18}	"	20.27
C_{19}-C_{28}	"	7.66

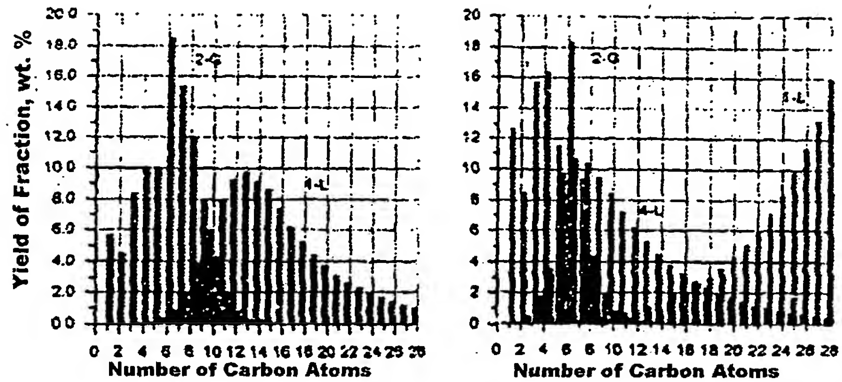

Fig. 2a,b

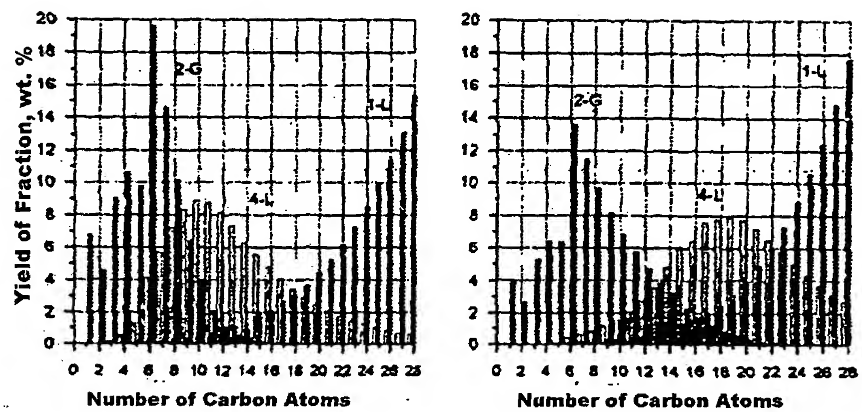

Fig. 3a,b